Thermochimica Acta, 24 (1978) 89–96
© Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

PROPERTIES OF MOLTEN CARBOXYLATES
PART 6. A QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS STUDY OF PHASE TRANSITIONS IN SOME ZINC AND CADMIUM CARBOXYLATES

I. KONKOLY-THEGE AND I. RUFF
Institute of Inorganic and Analytical Chemistry, L. Eotvos University, Budapest (Hungary)
S. O. ADEOSUN AND S. J. SIME
Chemistry Department, University of Ife, Ile-Ife (Nigeria)

ABSTRACT

Quantitative DTA results are presented for the phase changes in some cadmium and zinc n-alkanoates. Cadmium carboxylates form liquid crystal phases. The total entropy of the solid-to-liquid transition is small indicating a high degree of aggregation in the isotropic liquid. The phases previously reported by Skoulios et al. are shown to be due to the presence of basic carboxylates. The zinc carboxylates have solid–solid transformations but do not form liquid crystal phases. The entropies of fusion are of the same order as those in the lead salts showing only a small degree of aggregation in the liquid.

INTRODUCTION

In a previous paper in this series[1], we reported a quantitative DTA study of phase transitions in the even chain-length lead(II) carboxylates. The results were characterized by the formation of liquid crystalline phases between the crystal and isotropic liquid. Carboxylates from hexanoate to dodecanoate inclusive formed two such phases which were interpreted as being a laminar G (smectic) phase and a cubic isotropic V_2 phase. For the tetradecanoate-to-octadecanoate inclusive, only the G phase was present. The entropy of the V_2-to-liquid transition was consistent with the melting of a globular solid if the aggregates consisted of about three or four molecules of the carboxylate. This supported the model previously proposed on the basis of the chain-length dependence of the activation energy for viscous flow in these systems[2]. Viscosity measurements on the cadmium carboxylates[3], however, show a large activation energy, the variation with chain-length suggesting a single carboxylate moiety (RCO_2^- or RCO_2Cd^+) as the unit of flow. This is consistent with the infinite cylindrical micellar model proposed by Spegt and Skoulios[4] on the basis of their X-ray studies of the mesophases formed by their cadmium carboxylates. However, the melting points of the carboxylates used in our study (ca. 380 K), for which purity was checked by both elemental analysis for carbon and hydrogen and by IR spectroscopy, were much lower than those reported by Spegt and Skoulios (ca. 480 K). As these workers did not recrystallize their materials and "purified" them by boiling in water, it was suggested that they were in fact basic carboxylates[3], probably of uncertain composition. This was supported by a recent study in this series[5], in which it was shown that the addition of lead (II) oxide to lead dodecanoate at above 0.14 mole fraction caused the appearance of a new liquid crystalline phase at higher temperatures which coexisted with the isotropic liquid over a relatively large temperature range. Skoulios reported that the mesophase observed in his study showed this behaviour, in contradiction to the phase rule for a pure substance. In the present work, we present data for the formation of mesophases in pure samples of the cadmium carboxylates and report the effect of added cadmium oxide on mesophase formation.

Spegt[6] has reported, on the basis of X-ray data, that zinc soaps do not exhibit liquid crystal phases; however, there have been no quantitative DTA work on these materials and so, such studies are reported here.

EXPERIMENTAL

The preparation and purification of the carboxylates have been reported elsewhere[3, 6]. Cadmium oxide was prepared by roasting the carbonate at around 700 K. Measurements were performed at two centres; at L. Eotvos University, Budapest, measurements were made on a DuPont 990 thermal analyser with DSC module (N.B., this is a quantitative DTA instrument); at the University of Ife, the Mettler TA 2000 system was used. The DuPont instrument was used for the major part of the study of the zinc carboxylates, the Mettler instrument for the study of the cadmium carboxylates. A check for consistency between the two instruments was made by repeating some of the measurements on the zinc soaps using the Mettler instrument. Results from the two centres agreed to within experimental error. Areas of peaks were estimated either by planimetry (Budapest) or by cutting out and weighing (Ife). Calorimetric data for the zinc carboxylates are averages of runs performed at scan speeds between 0.5 and 5 K min^{-1}. For the cadmium carboxylates, calorimetric data are averages of runs performed at 1 K min^{-1}. All data are averages of at least 5 separate samples.

RESULTS AND DISCUSSION

The cadmium carboxylates

Detailed studies were performed only on the dodecanoate and longer chain-length soaps. The decanoate gave broad, ill-defined DTA peaks. The carbon and hydrogen figures for this compound[3] are about 1 % lower than the theoretical value, which may indicate the presence of inorganic cadmium impurities. It has been previously reported[3] that attempts to make the octanoate and hexanoate always

TABLE 1

THERMODYNAMIC DATA: CADMIUM CARBOXYLATES

Chain length	Crystal → Mesophase(1)			Mesophase(1) → Mesophase(2)			Mesophase → Liquid			Sum		Specific heats of liquid (J K^{-1} mol^{-1})	
	T (K)	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	T (K)	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	T (K)	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	Cd	Pb
12	367.7	13 ± 3	35 ± 1		Absent		370.5	8.6 ± 3.3	23 ± 9	23 ± 4	62 ± 11	909 ± 51	1080
14	374.7	43 ± 1	115 ± 3		Absent		380.4	1.6 ± 1	4 ± 3	44 ± 2	117 ± 5	1220 ± 30	1320
16	380.4	23 ± 6	60 ± 16	387.1	15.3 ± 1.3	40 ± 4	399 (broad)	4.8 ± 0.8	12 ± 2	47 ± 2	122 ± 5	1400 ± 15	1420
18	380[a]	19.6 ± 1.0	51 ± 3	386.2	22.8 ± 1.3	59 ± 3	391.2	26.2 ± 1.1	67 ± 3	68.2 ± 1.7	177 ± 4	1500 ± 15	1440

[a] Two superimposed peaks at approximately 381.7 and 379.2 K.

resulted in basic carboxylates. The enthalpy changes for the individual phase transitions were irreproducible; however, the total enthalpy change for crystal-to-liquid was reasonably reproducible. Similar behaviour has been observed in lead oxide–lead dodecanoate mixtures[5]. Numerical data are shown in Table I. Samples were left overnight before rerunning; however, in some cases, in particular the hexadecanoate, this annealing time was not sufficient, and reproducible data were only obtained if the samples were left for two or three days. Specific heats of the liquid phase were obtained by the method of baseline displacement and are shown in Table I.

Visual observation under a polarising microscope was of little help in distinguishing the phase type. On heating, no sharp visible signs of mesophase formation were observed at the phase transition temperatures. Above the temperature of the first transition, the materials became translucent and birefringent and finally became isotropic at, or just above, the temperature of the final phase change. In some samples, particularly of the dodecanoate, traces of birefringence were observed up to 15 K above the temperature of the final phase change. On cooling from the isotropic liquid, a smeared smectic-like texture was formed. The material was easily supercooled and no obvious changes in texture were observed at the temperatures at which the phase transitions were expected.

The irreproducible behaviour in the magnitudes of the heats of individual phase transitions, and the occurrence of birefringence up to 15 K above the temperatures of the final detectable phase change suggest that the samples still contain inorganic cadmium impurities. That this can occur even in recrystallised samples for which carbon and hydrogen analyses agree to within experimental error with the theoretical values is a striking illustration of the effects of relatively small amounts of impurity on mesophase formation in metal carboxylates, and must cast doubt on results obtained on materials for which purity has not been established. The fact that the materials used in this study were recrystallised from benzene must imply that the carboxylate is able to solubilise inorganic cadmium salts (oxide, hydroxide or carbonate) in benzene. If the impurity is hydroxide or carbonate, then it must be at a concentration below the level of detection by infrared spectroscopy.

The most striking feature of the quantitative results is the relatively small values of the total enthalpy (hence entropy) change from the crystalline-to-isotropic liquid phases. For the dodecanoate for example, the value of 23 kJ mol^{-1} must be compared with a value of 79 kJ mol^{-1} for lead dodecanoate[1] and 64 kJ mol^{-1} for zinc dodecanoate. This must imply a considerable amount of residual order in the carbon chain in the liquid cadmium carboxylates. It is interesting to compare the value of the entropy change on melting per mole of hydrocarbon chain in cadmium dodecanoate (31 J K^{-1} mol^{-1}) with that in the lead oxide–lead dodecanoate mixtures at high lead oxide concentration (23 J K^{-1} mol^{-1} at 0.3 mole fraction PbO; 49 J K^{-1} mol^{-1} at 0.16 mole fraction PbO; 107 J K^{-1} mol^{-1} for pure lead dodecanoate). As was pointed out in the case of these mixtures, these observations are consistent with a cylindrical micellar structure for the liquid phase in which packing requirements close to the core of the micelle impose spatial restrictions on the motion of the first few carbon

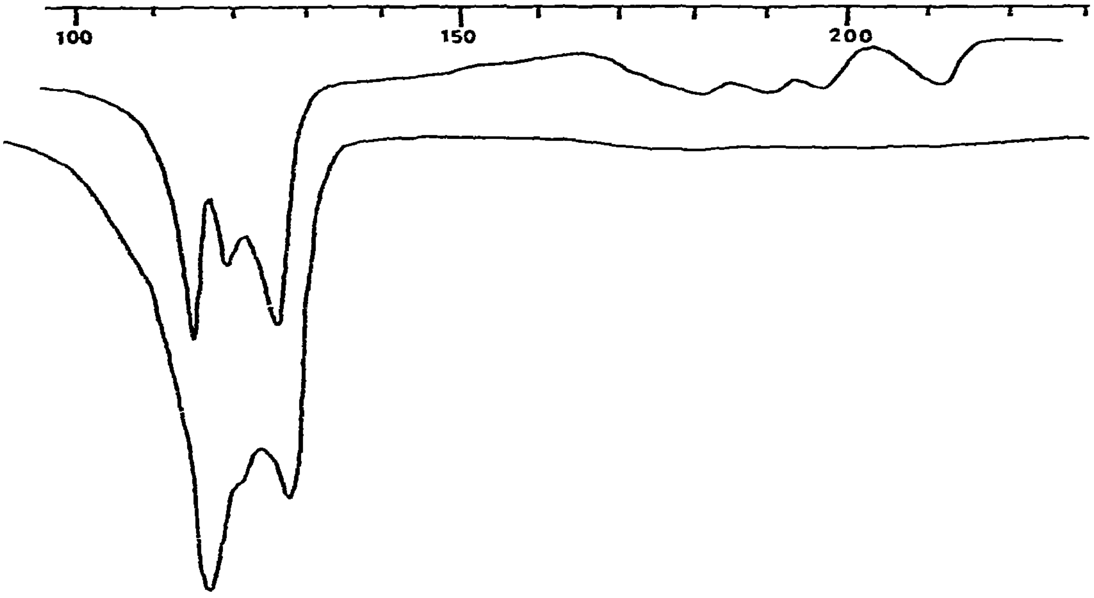

Fig. 1. DTA curves for pure cadmium octadecanoate (lower curve) and cadmium octadecanoate saturated with cadmium oxide (upper curve). The curves were recorded at a scan speed of 5 °C min^{-1}. Abscissa, temperature of the furnace wall (°C).

atoms of the carbon chain. One would have expected in such a case to observe a different specific heat of the cadmium carboxylates from that of the lead for the liquid phase. Unfortunately, the results show little significant difference between the liquid specific heats (Table 1).

To study the effect of added CdO on mesophase formation, the octadecanoate was chosen. This shows the largest difference in melting point: Skoulios observing 500 K, this work giving 391 K. Cadmium oxide is not easily soluble in cadmium octadecanoate; however, a sample of the soap was saturated with cadmium oxide by repeated melting and grinding and the DTA curve shown in Fig. 1 was obtained. Broad phase changes are observed between 430 and 470 K and another phase change at about 480 K. This corresponds well with Spegt and Skoulios'[4] observation of a phase between 370 and 470 K and a final phase between 480 and 500 K. It thus seems certain that the materials studied by these authors were basic carboxylates, although their proposed cylindrical micelle model is still consistent with the properties of the isotropic liquid in the pure carboxylates. It is possible that the presence of cadmium oxide increases the strength of ionic interaction in the micelle, favouring longer micelles and hence stabilising the hexagonal arrangement of infinite cylindrical micelles in the liquid crystal. In this case, we would view the pure liquid carboxylate as consisting of shorter cylindrical micelles arranged at random and possibly entangled. This would account for the abnormally high value of the viscosity of these compounds[3] compared to the zinc and lead compounds.

The zinc carboxylates

Several phase changes are observed on heating the zinc carboxylates. Optical examination shows that all these transitions are simple solid–solid transformations, no liquid crystalline phases being formed. Results on first heating differed slightly from results on premelted samples, possibly due to partial supercooling of high temperature solid phases, or possibly due to different crystal phases being formed on cooling than on recrystallisation from benzene. Quantitative heats for the phase transitions are shown in Table 2. Data are included only for the major peaks, other minor peaks being small and irreproducible. Values for overlapping peaks were separated by Gaussian analysis. Although, theoretically, quantitative DTA peaks should not be Gaussian, it was found that, on using the DuPont instrument, isolated

TABLE 2

THERMODYNAMIC DATA: ZINC CARBOXYLATES

Chain length	*Crystal → Crystal (A)*		*Crystal → Crystal (B)*		*Crystal → Liquid (C)*		
	T (K)	*ΔH (kJ mol⁻¹)*	*T (K)*	*ΔH (kJ mol⁻¹)*	*T (K)*	*ΔH (kJ mol⁻¹)*	*ΔS (J K⁻¹ mol⁻¹)*
6	353	7 ± 2	378	6.4 ± 0.6	418	26 ± 3	62 ± 7
8	373	1.4 ± 0.3	379	9.2 ± 0.1	413	43 ± 2	104 ± 5
10	372	2.1 ± 0.5	378	3.8 ± 0.8	407	49 ± 5	120 ± 12
12	372	1.0 ± 0.3	—	—	407	64 ± 3	157 ± 7
14	—	—	—	—	407	86 ± 6	211 ± 15
16	—	—	—	—	407	93 ± 10	229 ± 25
18	—	—	—	—	403	103 ± 7	256 ± 17

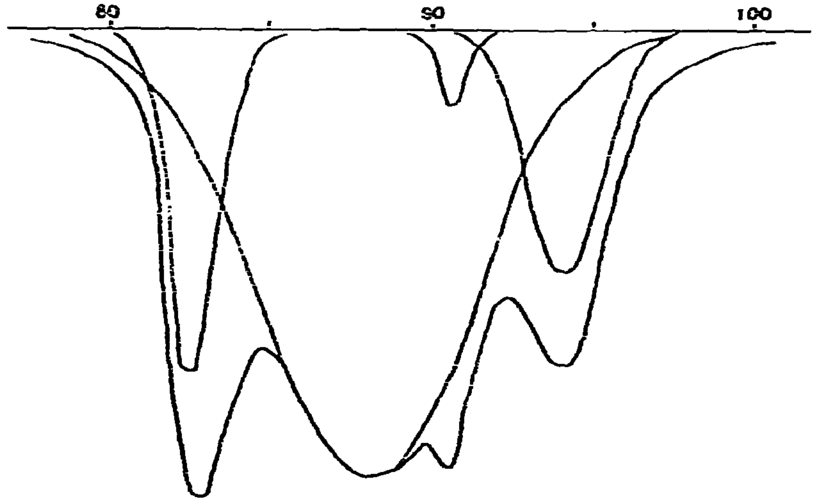

Fig. 2. DTA curve for zinc hexanoate at a scan speed of 2°C min⁻¹, showing decomposition into Gaussian components.

peaks were good Gaussians, and that composite peaks could be easily resolved into Gaussian components (Fig. 2). This was not true for the Mettler instrument in which the peak shape of single peaks corresponded more closely to the theoretical shape. Approximate Gaussian behaviour may be expected when the decay time for the DTA peak is of the same order as the rise time for the peak from the baseline. This will occur most easily for small heat effects in small samples on instruments with high thermal resistance between the sample and reference pans and the furnace wall. Near Gaussian behaviour will also be favoured by samples with small degrees of impurity rather than ultra pure samples. Although the assumption of Gaussian behaviour is not strictly valid, it does provide a self-consistent way of decomposing overlapping peaks, and, if isolated peaks in the same sample are Gaussian, then Gaussian analysis probably provides a more valid way of separating heat effects than visual extrapolation.

On first heating, many samples showed occasional "exothermic" peaks just before final melting, similar to those observed by Vold et al.[7] in the DSC curves of lithium hexadecanoate. These workers suggested that these were due to poor thermal contact between the powdered material and the pan, and this is supported by the fact that they are not usually observed in premelted samples.

It is pointless to speculate on possible structures for these different solid phases without X-ray evidence, although, if the structures of the solid phase are essentially laminar, it is possible that they are related to changes in the angle of tilt of the carbon chain to the ionic layer as is observed in the different polymorphic forms of the fatty acids[8].

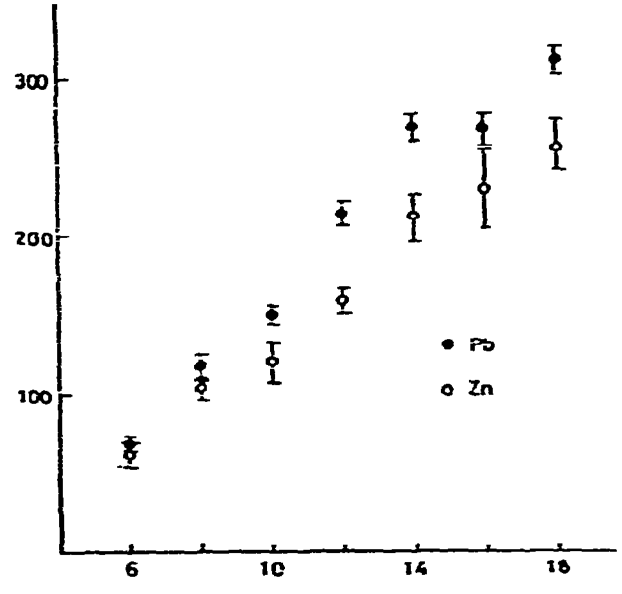

Fig. 3. Entropies of fusion for zinc and lead carboxylates. Abscissa, chain length; ordinate, ΔS ($J\ K^{-1}\ mol^{-1}$).

In Fig. 3 are plotted the entropies of fusion of the zinc carboxylates together with those for the change solid-to-isotropic liquid in the lead carboxylates. It can be seen that the values for these two series of compounds are compatible, supporting the idea, suggested by viscosity data, that the state of aggregation in these liquids is similar. The smaller values for the zinc carboxylates probably suggest that the solid–solid phase transitions involve some disorder of the paraffin chain prior to melting.

REFERENCES

1 S. O. Adeosun and S. J. Sime, *Thermochim. Acta*, 17 (1976) 351.
2 U. J. Epke and S. J. Sime, *J. Chem. Soc. Faraday I*, 72 (1976) 1144.
3 S. O. Adeosun, W. J. Sime and S. J. Sime, *J. Chem. Soc. Faraday I*, 72 (1976) 2470.
4 P. A. Spegt and A. E. Skoulios, *Acta Crystallogr.*, 16 (1963) 301.
5 S. O. Adeosun, W. J. Sime and S. J. Sime, *Thermochim. Acta*, in press.
6 M. E. Ekwunife, M. U. Nwachukwu, F. P. Rinehart and S. J. Sime, *J. Chem. Soc. Faraday I*, 71 (1975) 1432.
7 M. J. Vold, H. Funakoshi and R. D. Vold, *J. Phys. Chem.*, 80 (1976) 1753.
8 R. T. O'Conner, in K. S. Markley (Ed.), *Fatty Acids*, Vol. 1, Interscience, New York, 1960.